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Review

Analytical detection methodologies for methane and related hydrocarbons

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Abstract

The determination of methane is of strong interest to the analytical community due to its natural abundance, its potential to cause explosions and its known greenhouse effect. The current report gives a brief overview into the environmental significance of methane and an account of the existing detection protocols for methane in air and environmental samples.

Keywords: Methane; Hydrocarbon; Analytical; Review; Detection

Contents

1. Introduction

Methane is found in several environmental, industrial and domestic areas. It is the main constituent of natural gas, the fuel which is supplied to many domestic homes and industries, is often released from the walls of coal mines and when unmonitored can accumulate, causing dangerous explosions. Along with CO_2, NO and the halocarbons, methane is an important greenhouse gas, which has both natural origins, being continuously released by the anaerobic oxidation of organic materials or leaking from methane hydrate deposits; or anthropogenic origin such as the production of fossil fuels, leakage from landfills

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Table 1
A table detailing the detection limits and linear ranges achievable using the various detection methodologies

Technique	Sample	Detection range	Detection limit	Reference
Mid IR	Air	N/A	170 ppm	[11]
Mid IR	Air	N/A	2 ppb	[16]
Mid IR	Air	N/A	2 ppm	[16]
Near IR	Air	N/A	2.5 ppm	[17]
Mid IR	Air	N/A	105 ppt	[19]
Mid IR	Air	N/A	2%	[20]
Near IR	Air	N/A	30 ppb	[23]
Near IR	Land fills	N/A	5 ppm	[24]
Near IR	Air	0.2–100%	0.2%	[25]
Near IR	Air	N/A	20 ppbv	[26]
CRD	Air	N/A	52 ppbv	[27]
CRD	Air	N/A	4.0 ppb for ethene	[29]
Photoacoustic	Air	N/A	20 ppm	[33]
Electrochemical	Air	6–100 ppm	6 ppm	[49]
Biosensor	Aqueous	0–1 atm	1 μM	[50]
Biosensor	Rice paddy	N/A	1 μM	[51]
Solid state	Air	N/A	Tested 2000 ppm	[54]
Solid state	Air	>4150 ppm	N/A	[56]
Solid state	Air	N/A	100 ppm	[58]
Solid state	Air	0.02–5.5%	0.02%	[59]
Solid state	Air	N/A	0.1%	[67]
Solid state	water	N/A	0.55 ppm (0.075 nM)	[69]
Solid state	Air	N/A	500 ppm tested	[72]
Solid state	Air	0–500 ppm	N/A	[76]
Solid state	Air	0.01–5.5%	0.01%	[77]
Solid state	Anaerobic	1–20%	N/A	[79]
Calorimetric	Air	0–2.5%	>0.125%	[87]
Calorimetric	Air	N/A	Tested 1%	[89]
Calorimetric	Air	N/A	Tested 0.5% CH_4	
0.2% C_3H_8	[90]			
Calorimetric	Air	0.25–300 ppmv	0.25 ppm/v	[92]
Piezoelectric	Air	N/A	0.018 vol%	[93]
GC–FI	Air	1 ppm–100%	1 ppm	[95]
GC–PDHI	Human breath	0.3–400 ppmV	0.3 ppm	[97]
GC–FI	Air	N/A	35 ppbC, non-methane carbon	[98]
GC–FI	Air	N/A	0.15 μg/L	[100]
GC–PA	Air	N/A	1 ppbv	[101]

N/A, non-applicable; CRD, cavity ring down; PA, photoacoustic; GC, gas chromatography; FI, flame ionization; PDHI, pulsed discharge helium ionization.

or production by domestic animals. Therefore the detection of this potent gas is essential in the environmental, industrial and domestic worlds. There are clear benefits in extending our understanding of the methane cycle given its environmental impact. The dangers of methane can be averted by using sensors, that can operate over wide concentration range. The bulk of this review will analyze how this problem has been overcome. The review will be split into sections each detailing a different analytical technique and how its been utilized in the determination of methane and related hydrocarbons. Table 1 details an overview of the detection limits and ranges achievable with the various detection strategies described.

1.1. *What are its origins?*

At room temperature and low concentrations methane is a colorless, odorless gas yet at higher concentrations a sweetish chloroform-like odor is noticeable. It has a melting point of −184 °C and a boiling point of −164 °C. Methane is primarily formed by the anaerobic decay of organic matter by methane producing bacteria, which occur in air-less environments such as marshes, the guts of some animals and landfills. Methane is also trapped in pockets of the earth's crust, and can be released during the mining of fossil fuels. In the UK the major sources of methane from human activity are waste disposal, agriculture, coal mining and leakage from the gas distribution system. In 1996 Landfill sites accounted for an estimated 46% of the UK's methane emissions, whilst the second largest source of emissions was from the agricultural sector, principally from the grazing of livestock and animal wastes [1].

As stated above it can also be formed in the walls of coalmines and when mixed with air in the 5–15% level an explosive mixture known as firedamp results. There has also been evidence of the presence of methane within the 'Martian atmosphere' [2]. Using a Fourier transform spectrometer, Krasnopolsky et al. detected 'Martian methane'. They concluded that methanogenesis by living subterranean organisms upon Mars is a plausible explanation for its presence.

The emission of methane from humans occurs via the breakdown of carbohydrates, due to the action of anaerobic methanogenic bacteria, in the colon. Understanding the production of methane and other chemical species (e.g. H_2, CO_2, butyrates, indol) within the body could be a useful tool in the diagnosis and treatment of some gastrointestinal disease. Therefore a sensor capable of detecting methane within air exhaled from a patient will have clinical importance for near patient monitoring [3].

Methane is manufactured in an industrial process termed 'Methanation'. This is the process by which carbon monoxide (CO) and/or carbon dioxide (CO_2) are converted to methane by a catalytic reaction with hydrogen. This is usually conducted over a nickel catalyst heated to 230–250 °C and requires one volume of CO for every three volumes of hydrogen. Methanation is conducted for a variety of reasons, including removal of highly toxic CO from the gas stream in ammonia synthesis, purification of hydrogen by removal of CO and conversion of CO and hydrogen to methane, which increases the calorific value in town gas [4].

1.2. Chemistry

Although methane reacts explosively with chlorine, it is in essence a fairly chemically inert species. This low reactivity therefore makes its detection difficult for strategies that rely upon its derivatization for sensing. Therefore as will be shown below a significant number of the detection strategies utilise specific attributes of the molecule for its detection, for example its absorbance spectra in the infrared [5].

1.3. Health and environmental impact of methane

Although methane cannot be adsorbed into the skin or ingested it can be easily inhaled into the body. If inhaled, methane effectively replaces the oxygen in the body, causing suffocation. At low dosage levels the patient or worker may feel some dizziness or headaches that can be accompanied with nausea as the levels rise. At higher levels loss of consciousness and ultimately death will result [6]. The odorless nature of the gas makes it a danger to human health and hence is why domestic gas often has low levels of ethanethiol added (an odor gas) to make the user aware of gas leaks, due to its high explosive risk.

Methane is the second most important greenhouse gas (after carbon dioxide) resulting from human activities and releasing it to the atmosphere is thought to contribute to global warming. Upon release to the atmosphere it is destroyed by chemical reactions with other chemical species and therefore only has a comparably short lifetime of 10 years, compared to carbon dioxide, which can stay in the atmosphere anything from 50 to 200 years [1]. Over the last two centuries, methane levels in the atmosphere have increased two-fold, predominantly due to human activities. Recent concerns over the impacts of methane on global warming (it has a much greater warming effect on the climate than carbon dioxide) have resulted with steps being undertaken to decrease the human induced emissions [1]. Due to its effects on global warming it has also been included in the United Nations Framework Convention on Climate Change (UNFCCC) Kyoto Protocol for reporting requirements [7].

Locally, methane gas build-up has the potential for causing explosions; this has resulted in temporary evacuations of residents where the housing estates were built on top of old landfill sites that had not been sufficiently vented of methane [1].

2. Detection methodologies

Detailed below is an overview of the various analytical techniques developed since 1990, used in the detection of methane. Table 1 details the analytical parameters achievable using the various detection methodologies.

2.1. Spectroscopic detection

2.1.1. Infrared

The principle of diode laser spectroscopy as a means of sensing variations in gas concentrations is based upon its ability to detect the absorption line. This has significant advantages in terms of sensitivity and selectivity, as the absorption lines are usually a unique feature of the gas under detection. The entire spectral range from the visible to the IR can be covered by using semi-conductor lasers based upon gallium-arsenide, indium phosphide, antimonides and lead salts. A typical experimental set-up for the spectroscopic determination of methane is detailed in Fig. 1. The near infrared (IR) lasers offer an advantage over their mid IR counterparts as they do not require expensive cooling equipment, however, in this range most of the molecules of interest only have overtones and combinational bands which have lower absorption strengths in comparison to the mid IR range. Therefore selection of the optimum operating conditions for analysis has to take into consideration both the required sensitivity (mid IR is more sensitive) and the ability to operate the system (near IR is easier to operate). The ability to predict sensitivities is relatively facile in the laboratory with knowledge of the line strengths, however, in the field, difficulties occur due to drift effects and other such problems [8]. To overcome these inherent tribulations approaches based upon signal processing [8] and double modulation techniques [9] have been employed.

In the mid IR range, methane gives a signal at 3.3–3.4 μm, which has been successfully detected using light emitting diode (LED)-photodiode pairs [5,10–17]. A typical spectrum recorded with an optical path length of 1 mm at 1.08 bar of pure methane (>99.998%) is detailed in Fig. 2. A publication by K. Strong et al.

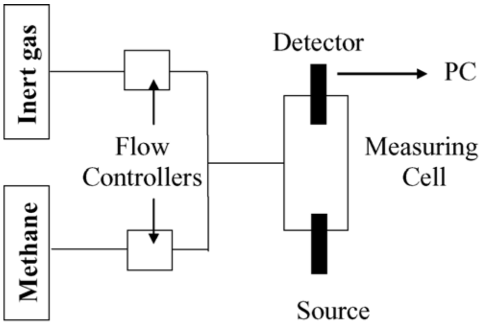

Fig. 1. A typical experimental set-up for the monitoring of methane in a spectroscopic cell.

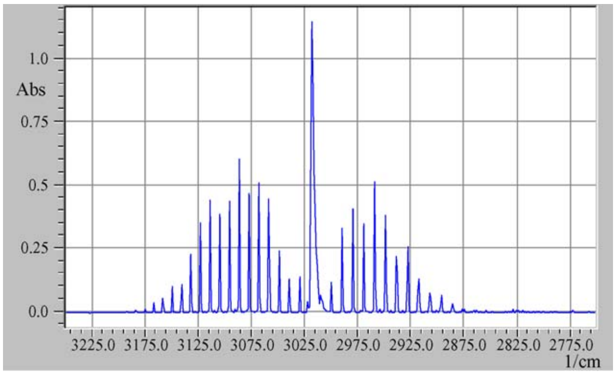

Fig. 2. A typical mid IR spectrum of pure methane (1.08 bar, 99.998%) recorded with an optical path length of 1 mm at 26 °C.

details a comprehensive summary of the principal infrared CH_4 bands [18]. It was found that detection limits as low as 170 ppm could be reached when using an InAs photodiode-InGaAs pair with a single LED pulse of $I = 3$ A, $\tau = 10$ μs at room temperature (Table 1) [11]. Furthermore cavity leak out spectroscopy [19] has been utilized for methane detection at 3.39 μm in the mid IR region.

A novel approach has relied upon coating the optical fiber core with a transparent polymer whose refractive index is modified during adsorption of the methane species. In the case of methane the optical fiber was coated with two cryptophan molecules. Coating the surface with these species allowed detection limits of 2% (v/v) to be obtained [20].

Near IR signals take advantage of the methane band around 1.65 μm in order to detect the gas. Diode lasers [21,22] are the common tool for measuring the signal and are often constructed of various GaAs compounds including; GaInAs [23] and InGaAsP [24,25]. Techniques which make use of these continuous wave diode lasers include direct adsorption spectroscopy with long path lengths [26], cavity ring down spectroscopy (CRDS) [27–29], cavity enhanced spectroscopy [30], integrated cavity output spectroscopy [31] and photoacoustic sensors [32,33].

2.1.2. Raman

Combined ‘smeared’ vibrational coherent anti-Stokes Raman spectroscopy (VCARS) and dual-broadband rotational CARS (DBB-RCARS) has been utilized for the simultaneous measurements of temperature and relative concentrations of O_2/N_2 and CH_4/N_2 in a fuel-rich CH_4/air-flame. A dye laser was tuned to the Q-branch transitions of methane with both VCARS and DBB-CARS signals generated and detected simultaneously. The relative intensity of the ‘smeared’ VCARS signal determines the relative concentration of methane and the residual DBB-RCARS signal measured the temperature and relative concentration of oxygen [34].

2.2. Electrochemical detection

2.2.1. Amperometic detection

Direct electrochemical oxidation of alkanes at an electrode surface has seen limited interest with the process requiring aprotic solvents with specific electrolytes [35,36] to obtain the required solvent window. Early research found that the use of perchlorate electrolytes did not give the wide potential window required to oxidize the hydrocarbons [37,38] and it was only when tetraflouroborates and hexaflourophosphates were introduced, which significantly increased the potential window of acetonitrile, that the anodic oxidation of various hydrocarbons could be analyzed [39,40]. Since then acetonitrile has been replaced with various acidic solvents including; CF_3COOH, FSO_3H, HF and CF_3SO_3H and even anhydrous HF under both basic (KF) and acidic (Sb_5F) conditions. The introduction and use of these compounds and other aprotic solvents have allowed further research to be undertaken into the electrochemical behavior of methane and other hydrocarbons [35,36,41]. Although the reaction mechanism is not entirely clear and often depends upon the solvent matrix a chemically irreversible voltammetric wave is often observed, consistent with electrochemical oxidation followed by subsequent homogeneous reactions of the newly formed product. This direct oxidation pathway has been utilized for the amperometric determination of methane, in which a Pt black-Teflon electrode was placed in contact with the organic electrolyte solution [42,43].

$$CH_4(gas) + Pt \rightarrow CH_4\text{-}Pt$$

$$CH_4\text{-}Pt \rightarrow CH_3\text{-}Pt + H^+ + e^-$$

Scheme 1.

Due to its high abundance in natural gas, methane has also been considered as an ideal candidate to be utilized in fuel cells, to produce electrical energy. As a consequence of this several research groups have focused on the ability of hydrocarbons to adsorb onto platinum surfaces, especially under acidic conditions with a Nafion coated surface [44–46]. It was found that under these conditions the hydrocarbon adsorbs slowly whilst undergoing a dissociation reaction (Scheme 1).

This adsorption process has since been employed as a ‘neat’ methodology of detecting methane. In this system a platinum electrode is deposited onto a Nafion-membrane such that it is in direct contact with the gas phase, and the membrane can act as both a mechanical support and a solid polymer electrolyte. The methane adsorbs onto the metal surface and the analytical signal is recorded by linear sweep voltammetry in the anodic direction [47]. In this case it is believed that the adsorbed methyl group reacts with water to form ‘CO-type’ species [48], which are completely oxidized to CO_2 in the anodic scan [45] (Scheme 2).

This affinity of methane to noble metals has recently been coupled with the electronic and structural properties of carbon nanotubes. In this case the single walled carbon nanotubes were loaded with palladium, which attracts electrons from the carbon nanotube. The methane then adsorbs onto the Pd, thereby increasing the current through the p-type carbon nanotube [49]. This type of conductance/resistance measurement has also been employed in conjunction with metal oxide semi-conductors (see Section 2.3).

$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^- + 8e^-$$

Scheme 2.

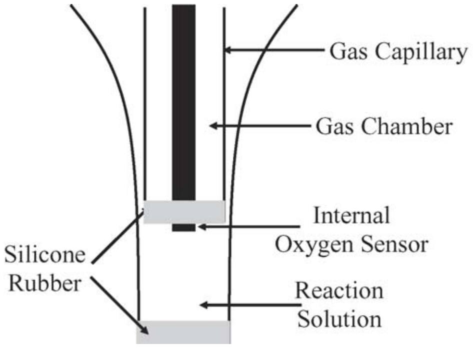

Fig. 3. A schematic design of the working area of the methane biosensor.

2.2.2. *Electrochemical biosensors*

A third type of electrochemical sensor is an indirect measurement based on the reaction of methane with methanotrophic bacteria [50,51]. A schematic of the cell design is shown in Fig. 3. In this case, an internal oxygen supply is present in the gas capillary to help drive the reaction. Upon the introduction of methane the methanotrophic bacteria oxidize the methane whilst concomitantly consuming oxygen. Measuring the change in oxygen concentration within the cell generates the signal. The initial design was found to be insensitive to hydrogen, ammonia carbon dioxide and acetate; however, both hydrogen sulfide and oxygen interfered with the signal [50]. The oxygen interference was overcome using of an oxygen guard electrode in a follow up design [51].

2.3. *Solid state*

Semi-conducting metal oxides have been utilized for the detection of gases due to their ability to alter conductance or resistance depending on the presence of various gases. The most common of these materials is tin oxide (SnO_2) [52–63], which is a wide gap semi-conductor and, due to the nonstoichiometric composition as a result of oxygen deficiency, has an n-type electrical conductance, which depends on the composition of the contacting atmosphere. Its ability to sense methane gas is due to a surface reaction between the methane and adsorbed oxygen. The oxygen chemisorbs onto the surface, thereby decreasing the concentration of electrons and increasing the electrical resistance. In the presence of methane, the gas detection mechanism involves the oxidation of methane with adsorbed oxygen to form CO_2 and H_2 (Fig. 4). This reaction consumes the oxygen on the surface, thereby increasing the conductance of the material [60]. However, due to the high stability of methane this process has to take place at temperatures above 400 °C to obtain the required sensitivity [64]. A further problem in using untreated SnO_2 is its low stability and lack of selectivity and its response is particularly affected by the presence of ethanol [54]. Therefore suitable filters, such as Al_2O_3 [62], SiO_2 [53] and zeolites [65] that contain noble metal catalysts [66–68] and/or dopants (Pd, Pt [59], Rh), are added to the tin oxide to increase the selectivity of the system. Furthermore, the detection process can be coupled with traditional separating techniques such as gas chromatography (see Section 2.6) to achieve the desired selectivity [69].

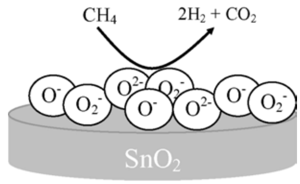

Fig. 4. A schematic diagram of the interaction of methane with a tin oxide electrode.

$$CH_4 + CO_2 = 2H_2 + 2CO$$

Scheme 3.

In order to overcome the issues of selectivity and stability associated with the bare tin oxide film, new sensor materials such as $BaSnO_3$ [70], Ga_2O_3 [71,72], CaZrO3/MgO [73,74], gold electrodes doped with Ta_2O_5 [75], and MnO_2 doped In_2O_3 [76] have been investigated. These also suffer from interferences such as ethanol, although when they are used at a sufficiently high temperature, selectivity can be achieved as other organic vapors are burnt off more readily than the methane [77,78].

A further drawback in employing the approaches outlined above is their requirement to have oxygen present, which would of course have significant limitations when detecting methane in anaerobic conditions. A new sensor has been developed which can measure levels of methane under such conditions [79]. This utilizes a catalytic asymmetrical Nernst-Type sensor [80,81] in which methane is converted into hydrogen, a detectable product [82–85] (Scheme 3).

The electrode set-up is detailed in Fig. 5, and basically employs two electrodes, each with a known catalytic activity towards hydrogen generation. In the presence of methane, a different quantity of hydrogen will be formed at each electrode surface setting up a change in the hydrogen partial pressure across the cell this variation, which can be manipulated to calculate the methane concentration. This set-up has some significant advantages, including the ability to quantify methane in the absence of air, a reference gas is not required and a simple construction with the possibility of miniaturization.

2.4. *Pellistors or calorimetric detection*

A pellistor is a type of calorimetric combustible gas sensor that employs the principle that when a heated catalytic element

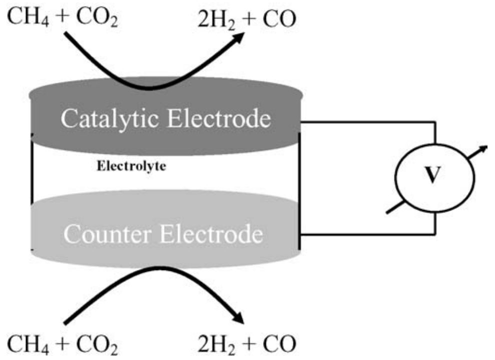

Fig. 5. A schematic diagram of the methane detector capable of operating in an anaerobic environment.

is exposed to a mixture of combustible gases a variation in temperature will be observed [86]. Modern pellistors usually consist of a wire coil embedded within a refractory bead loaded with a metal catalyst (usually Pd). The coil is used to heat the catalyst pellet to its operating temperature of ca. 550 °C. Concurrently, the metal coil is used to monitor any changes in heat produced by the combustion of the gases on the catalyst pellet. In order to decrease heat losses by conduction along the metal wire and to achieve reasonable sensitivity, the wire has to be thin making the device fragile. To overcome these problems, ‘micromachined hot plates’, have been introduced which effectively replace the wire [87].

Selectivity can be achieved by employing two noble metals with different catalytic activities towards methane oxidation (e.g. platinum and palladium [88]). At approximately 400 °C, methane and other hydrocarbons can be oxidized by palladium although only longer hydrocarbon chains, such as propane, can be oxidized at the platinum surface under the same conditions [88]. In fact to oxidize methane at a platinum surface temperatures up to 700 °C are required [89]. Therefore by use of a reference sensor the concentration of methane can be determined simply by examining the differences observed at each electrode [90,91]. Selectivity can be further achieved by use of a single pellistor when it is coupled with gas chromatography (Section 2.6) prior to detection [92].

2.5. *Piezoelectric sensors*

Piezoelectric sensors [93,94] as the name suggests are based upon the variation in the resonance of a quartz crystal in the presence of different gases. It has been shown that the ultrasound velocity in methane is different from that in air, thereby allowing its detection with a tunable gas sensor [93]. The sensor has been also found to respond to hydrogen with greater sensitivity as its presence has a greater affect on the ultrasound velocity than to methane [94]. However, rapid detection of both gases is still achievable and often depends upon the time for the gas to fill the detection cavity [94].

2.6. *Gas chromatography*

Gas chromatography [65,69,95–101] techniques have been applied to the detection of methane in a number of matrices including, environmental/effluent water [69,101,102], bore holes [95], human breath [97], paddy soils [102] and ambient air [98,100]. The separation capabilities of gas chromatography are obviously a significant advantage in complex media providing resolution between the different hydrocarbon gases and common gaseous interferences. In order to derive the analytical signal end column detectors are employed, which includes: conductivity [69], flame ionization [95,96,99,100], mass spectrometry [101], photoacoustic [102], pellistor [92] and pulsed helium discharge ionization detectors [97]. The use of the chromatographic separation technique along with the detector often allows low detection limits to be reached, although, the nature of the chromatographic set-up can be cumbersome when deploying the technique to field measurements.

2.7. *Commercial devices*

There are a number of commercially available methane sensors on the market, which are either often based upon solid state devices (Section 2.3) [103,104] or via optical methods (Section 2.1) [105,106]. In all these designs the sensor is usually placed behind a membrane in order to achieve both selectivity and the desired sensitivity for specified applications.

3. Conclusion

This review shows that there are a plethora of techniques or approaches that can be effectively varied to suit a given application. The attainment of adequate selectivity rather than sensitivity is one of the more pressing needs at present with the majority of techniques exhibiting a response to not only methane but also other hydrocarbon species. The needs to develop small sensing systems effectively rules out the incorporation of column separation on the grounds of manufacturing practicalities and therefore effectively leaves membranes as the main barrier against interferences.

Acknowledgement

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